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Dry development of resists exposed to low-energy focused gallium ion beam

Hiroki Kuwano
Musashino Electrical Communication Laboratory, Nippon Telegraph and Telephone Public Corporation, Musashino-shi, Tokyo 180, Japan

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This paper proposes a new lithography method employing focused ion beam exposure and subsequent dry development. It is shown that the O_2 plasma etching or reactive ion etching rate for resists exposed to gallium ions is much lower than that for resists not exposed. A comparison is made between plasma development and reactive ion development. An improvement in the resist sensitivity and contrast value γ using a $CF_4 + O_2$ mixture gas for reactive ion development is discussed. It is possible to fabricate 0.5-μm-width lines and spaces in 0.6-μm-thick PMMA film at 1×10^{-4}-C/cm^2 gallium ion exposure.

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I. INTRODUCTION

Electrons, x rays, and ions are being used to fabricate submicrometer patterns and high-level microcircuits and have led to various lithographic wafer applications. However, the electron beam and x-ray method have some problems relating to proximity effect and/or throughput.

Recently, there has been a growing interest in the applications of focused ion beams. Ion beams will become increasingly more important for submicron lithography of direct writing onto wafers and for mask fabrication. Resist exposure is more advantageous for such minute pattern fabrication, because the ion scattering inside the resist is less than electron scattering. Moreover, the focused ion beam can also be used for ion implantation, ion milling, and so on.

However, in the resist exposure, it is difficult to fabricate a pattern with practical thickness ($\gtrsim 0.5$ μm) by using low accelerated ions ($\lesssim 50$ kV).

To overcome this problem, the author proposes a new lithographic method employing a low-energy focused ion beam exposure and subsequent dry development.[1] Resist pattern fabrication with this method had been demonstrated by employing plasma development.[1] Furthermore, Venkatesan *et al.*[2] and Adesida *et al.*[3] demonstrated the possibility of fabricating a submicrometer pattern using this method.

In this paper, by using focused gallium ion beam exposure, a comparison is made between plasma etching (PE) dry development and reactive ion etching (RIE) dry development. Furthermore, an improvement in resist sensitivity and contrast value γ using a $CF_4 + O_2$ mixture gas for RIE development is discussed. Finally, submicrometer patterning using this method is shown.

II. EXPERIMENTAL PROCEDURE

The new lithographic method consists of two principal processes, shown in Fig. 1. The first is the exposure process using focused ion beams, and the second is the development process, in which PE or RIE is performed.

A. Exposure apparatus

Exposure was carried out with a prototype focused ion beam exposure system. Figure 2 shows a drawing of this ion beam exposure system. The liquid metal (Ga) ion source is a capillary needle type similar in concept to the type described by Clampitt *et al.*[4] A solid tungsten needle is wetted with gallium and supported in a reservoir tube. An intense positive potential, more than 4 kV with respect to the extraction aperture, is applied to the needle. Ion currents ranging from 5 to 100 μA are generated. The field at the ion-emitting point is contolled by the extraction voltage.

The lens column, consisting of an einzel-type objective lens and a Munro E type accelerating projective lens, is used to focus the submicrometer ion beam and to vary the probe current. Focusing can be achieved while watching the secondary electron image display. Secondary electrons are detected and amplified by a secondary electron multiplier in order to generate a microscopic image display.

An electrostatic deflector enables the beam to be scanned in the X and Y directions across a target. The scanned field is 500-μm square at a 20-kV acceleration voltage.

B. Dry development apparatus

PE development using a barrel-type rf (13.56 MHz) plasma etching system, and RIE development using an improved barrel-type (nearly parallel plate electrode type) system are shown in Figs. 3(a) and 3(b), respectively. The RIE

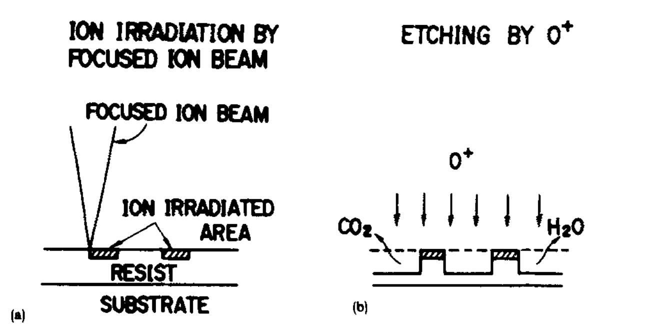

FIG. 1. New lithography method using focused ion beam exposure and subsequent dry development.

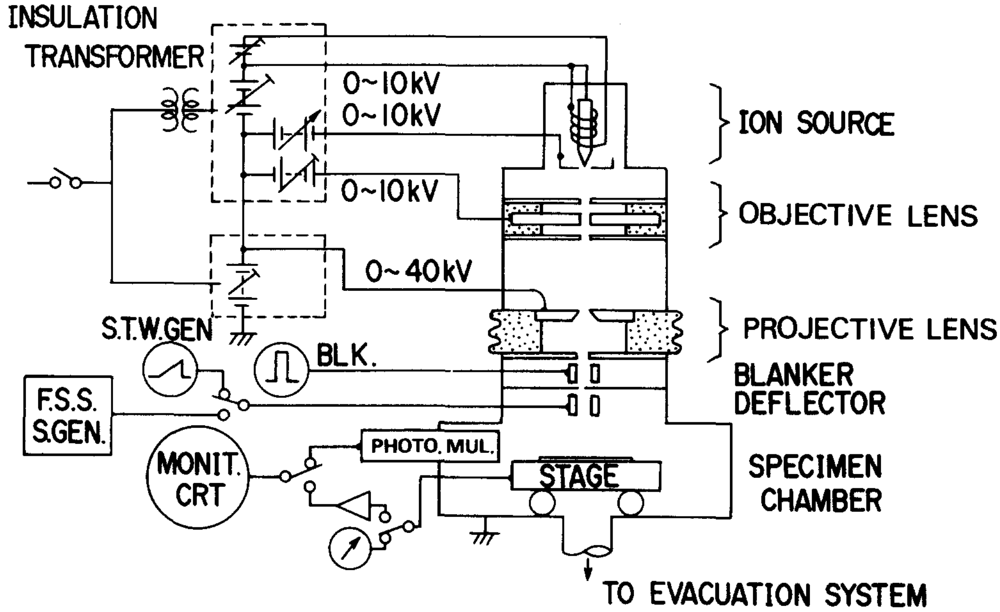

FIG. 2. Ion beam exposure system drawing.

system shown in Fig. 3(b), similar to that reported by Matsuo *et al.*,[5] is capable of applying a self-bias voltage to the specimen surface.

The differences in the etching characteristics between Figs. 3(a) and 3(b) are presumed to be basically due to the existence and the degree of incident ions on the specimen surface, accelerated by the self-bias voltage in the region of dark space in rf glow discharge.

III. RESULTS AND DISCUSSIONS

A. Comparison of PE development and RIE development

Figure 4 shows the O_2 PE depth for a poly methylmethacrylate (PMMA) resist exposed to about 20-kV accelerated gallium ions. In the experiment, a 1-μm-thick PMMA resist is used. During the etching, oxygen pressure is 0.7 Torr and rf power is 200 W, using the type A system.

It is proved that the etching rate for resists exposed to gallium ions differs from that for resists not exposed. The greater the gallium ion dose, the lower the etching rate becomes. For a 1.6×10^{-4}-C/cm^2 dose, the remaining thickness ratio is 85%, and for a 8×10^{-5}-C/cm^2 dose, the ratio is 45%. Figure 4 shows that PMMA resist functions as negative resist.

Figure 5 shows a PMMA resist pattern observed through a scanning electron microscope. After PE dry development, the resist pattern consists of two layers, as shown in Fig. 5(b). One is about a 200-Å-thick surface layer, where the resist is exposed by a focused gallium ion beam and has a masking effect against oxygen plasma. The other layer is not implanted by gallium ions and is easily side-etched by oxy-

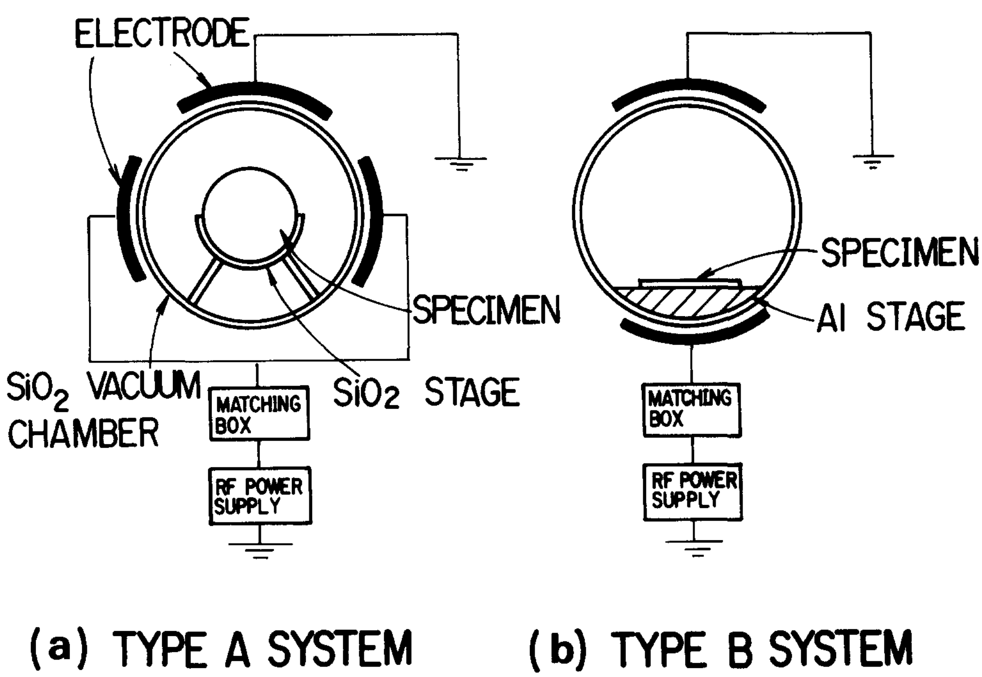

FIG. 3. Dry development system drawings. (a) Type A system; PE development. (b) Type B system; RIE development.

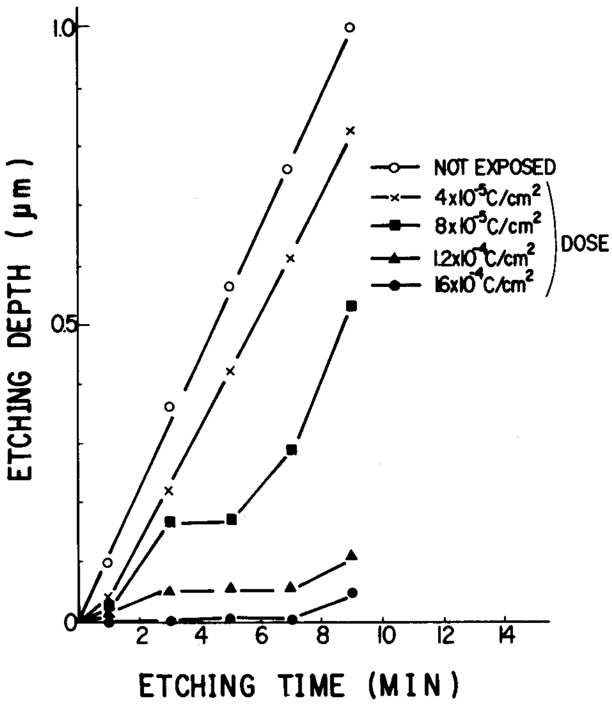

FIG. 4. O_2 plasma etching depths for a PMMA resist exposed to about 20-kV accelerated gallium ions. Etching conditions: oxygen pressure 0.7 Torr, rf power 200 W, using the type A system.

gen plasma. The x-ray photoelectron spectroscopy (XPS) analysis of this surface layer shows that, after dry development, this layer contains more Ga_2O_3 molecules than Ga atoms and that, before dry development, the layer contains more Ga atom than Ga_2O_3 molecules. It is thought that Ga atoms are changed to Ga_2O_3 by oxygen plasma.

The dry development mechanism is considered to be as follows. The area implanted by accelerated gallium ions in the thin surface layer of the resist is exposed by oxygen plasma. In this process, the gallium atoms in the surface layer of the resist change to Ga_2O_3 molecules. Thus, this layer has a masking effect against oxygen plasma. On the other hand, the unimplanted area is easily etched by oxygen plasma. By the above dry development process, the resist patterning is accomplished.

Figure 6 shows RIE depths for a 1-μm-thick PMMA resist exposed to about 20 kV of accelerated gallium ions using O_2 gas. In this etching process, which uses the type B system shown in Fig. 3(b), oxygen pressure is 0.3 Torr and rf power is 200 W. In the beginning, the etch rate for each resist exposed to gallium ions is small. After some etching time, however, the etch rate is nearly equal to that for a resist not exposed to gallium ions. This is the same as in the oxygen PE shown in Fig. 4. However, the remaining thickness ratio in the case of RIE is lower than that for PE.

Resist sensitivity curves for PE and RIE development are plotted in Fig. 7. In the experiment, 1-μm-thick PMMA resists were used. There are some differences among these three cases.

Both resist sensitivity (dosage for 50% normalized thickness remaining) and contrast value γ ($\gamma = \log D_0/D_i$, where D_0 is the dose for useful normalized thickness, and D_i is the dose for beginning image formation) become lower as oxygen gas pressure decreases. The sensitivity changes to 4.5×10^{-4} C/cm^2 from 9×10^{-5} C/cm^2 and the contrast value γ changes to 0.7 from 1.8.

The self-bias voltage applied to the specimen surface becomes high for low-pressure etching. Accordingly, the implanted region (having a masking effect against oxygen plasma) is physically sputtered by relatively high energy oxygen ions. This is why resist sensitivity and contrast value γ are small for low-pressure conditions.

Figure 8 shows resist sensitivity curves for several resist thicknesses. During development, oxygen pressure is 0.3 Torr and rf power is 200 W using the type B system. It is evident that a small thickness resist is advantageous for high sensitivity and high contrast value γ of the patterning.

In Fig. 9, sensitivity curves for several kinds of resists are shown. There are some differences among these curves. Sensitivity and contrast value γ for hexafluorobutyl-metha-

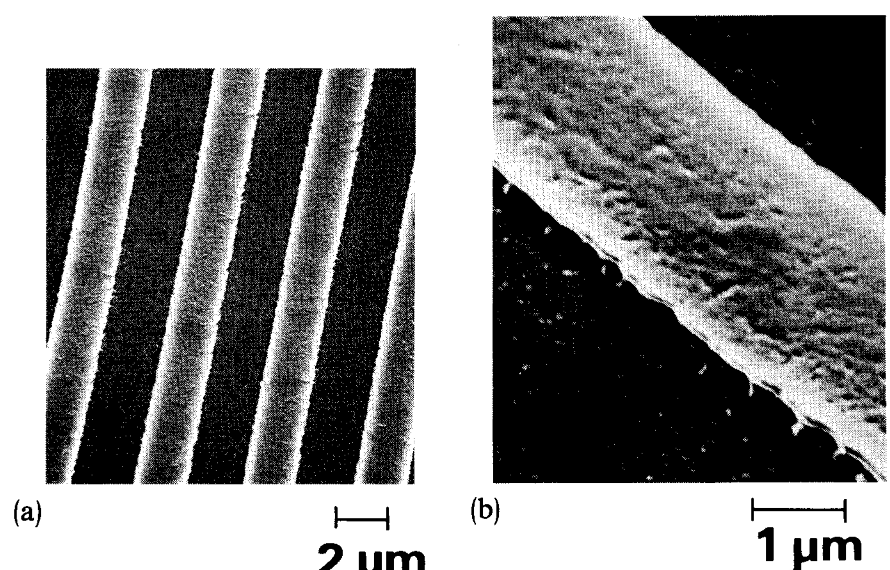

FIG. 5. SEM photograph of PMMA resist patterns fabricated by gallium ion beam exposure and subsequent oxygen plasma development. Development conditions: oxygen pressure 0.7 Torr, rf power 200 W, using the type A system. (b) is a magnified version of (a).

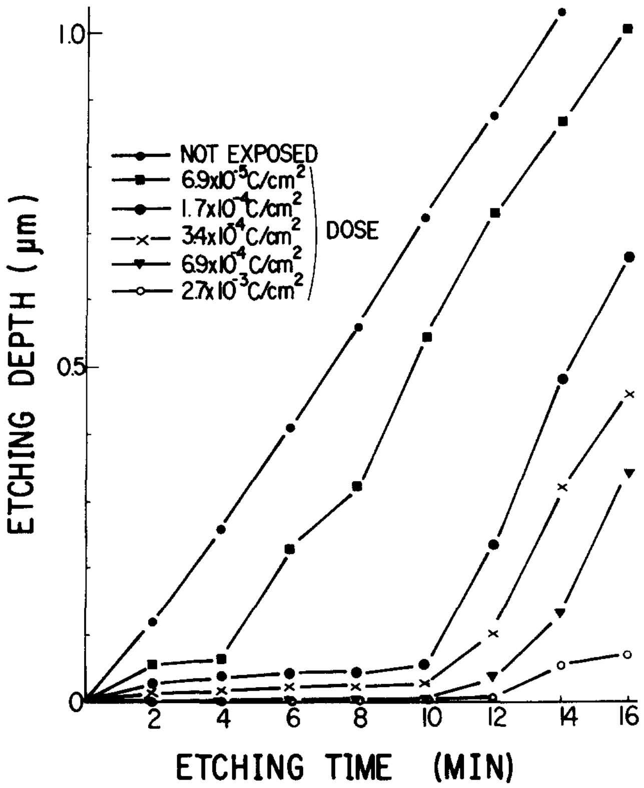

FIG. 6. RIE depths for PMMA resist exposed to about 20-kV accelerated gallium ions. Etching conditions; oxygen pressure 0.3 Torr, rf power 200 W, using the type B system.

crylate (FBM), whose plasma resistivity is relatively low, are the highest among these resists. However, the reason for this difference between resists is not clear.

B. Dry development using a $CF_4 + O_2$ gas mixture

In Fig. 10, the sensitivity curve for a 1-μm-thick PMMA film, in which a $CF_4 + O_2$ ($CF_4{:}O_2 = 1{:}1$) gas mixture RIE dry development method is applied, is compared with a curve in which only O_2 gas is used. When using a $CF_4 + O_2$ mixture gas, the dosage, which results in a 50% normalized thickness, is 8.3×10^{-5} C/cm^2. Moreover, the

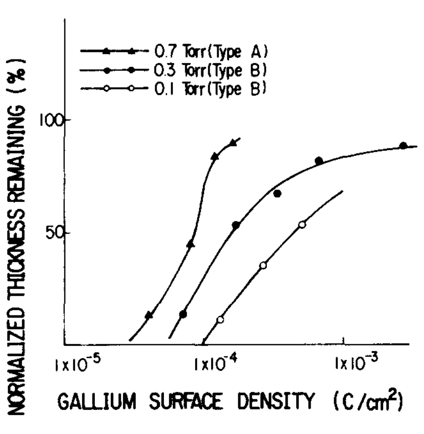

FIG. 7. PMMA resist sensitivity curves for oxygen PE development and RIE development.

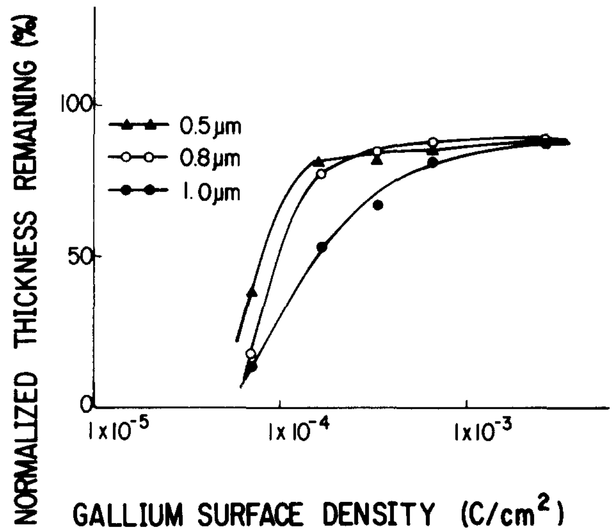

FIG. 8. PMMA resist sensitivity curves for several resist thicknesses. Development conditions: oxygen pressure 0.3 Torr, rf power 200 W, using the type B system.

resist sensitivity using a $CF_4 + O_2$ gas mixture is about five times as high as that using only an O_2 gas. Furthermore, contrast value using a $CF_4 + O_2$ gas mixture is 2.4 and 2.8 times as large as that using only an O_2 gas. From the resist sensitivity and contrast value standpoint, using a $CF_4 + O_2$ gas mixture is superior to using only an O_2 gas. Here, the resist etch rate using a $CF_4 + O_2$ gas mixture is about ten times as large as that using only an O_2 gas.

It is not clear why the resist sensitivity and the contrast value γ using a $CF_4 + O_2$ gas mixture are superior to those using O_2 gas only. It may be caused by a rapid resist etch rate

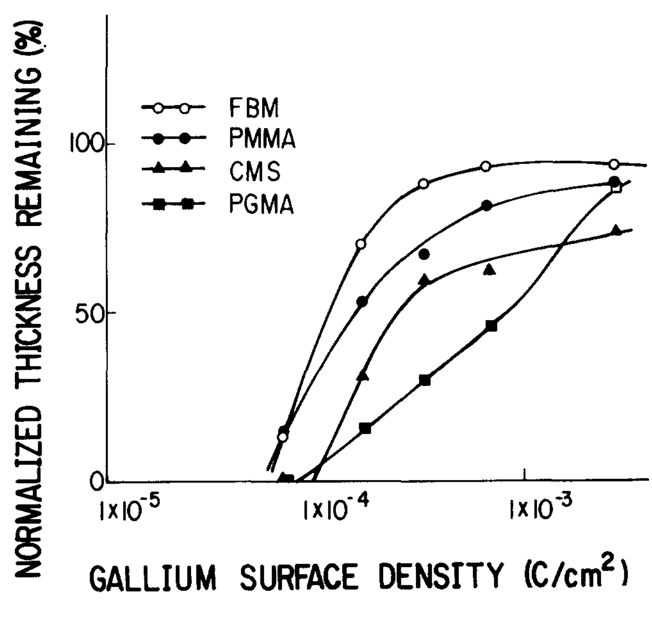

FIG. 9. Sensitivity curves for several kinds of resists. Development conditions: oxygen pressure 0.3 Torr, rf power 200 W, using the type B system. FBM: hexafluorobutyl-methacrylate; CMS: chloromethylated polystyrene; PGMA: poly glycidyl-methacrylate.

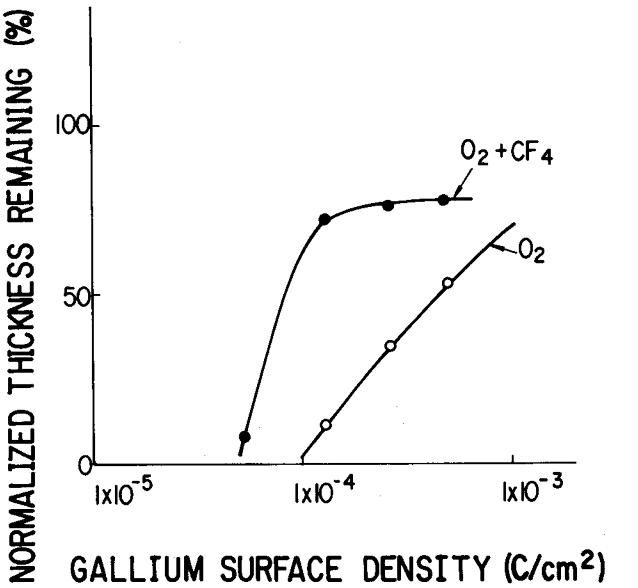

FIG. 10. Sensitivity curve for 1-μm-thick PMMA film. Development conditions: gas pressure 0.1 Torr, rf power 200 W, using the type B system.

for a $CF_4 + O_2$ gas mixture and the high resistivity surface layer (e.g., $GaF + Ga_2O_3$) for O_2 plasma.

Figure 11 shows normalized lateral etching rate (lateral etching rate/vertical etching rate) vs $CF_4 + O_2$ mixture gas pressure. In the experiment, a 1-μm-thick PMMA resist, exposed to 1×10^{-4}-C/cm^2 gallium ions, is dry developed by the type B method. The lower the pressure, the smaller the normalized lateral etching rate becomes. It should be especially noted that the etching rate for 5×10^{-2} Torr is about 0.1. The lateral etching rate is small when the gas pressure is lower. This is because the number of radicals F of CF_x having no directional effect is low and the self-bias voltage which accelerates incident ions to the specimen surface in the rf glow discharge dark space region is high.

Figure 12 shows several cross-sectional views of a PMMA resist. The large undercutting in Fig. 12(a) was done under 0.7-Torr $CF_4 + O_2$ and 200-W rf power conditions.

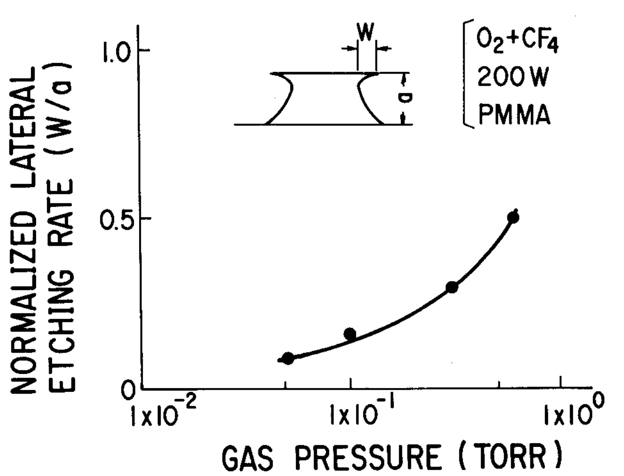

FIG. 11. Normalized lateral etching rate (lateral etching rate/vertical etching rate) vs gas pressure. A 1-μm-thick PMMA resist exposed to 1×10^{-4} C/cm^2 gallium ions was used.

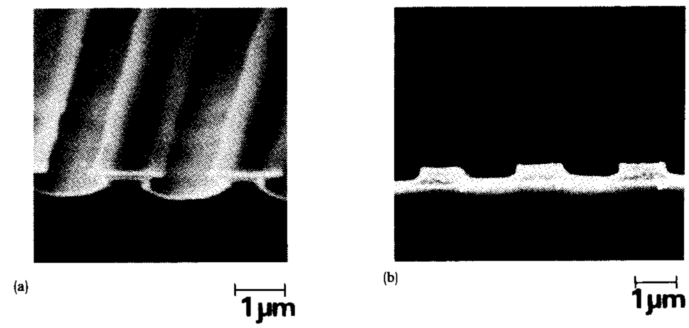

FIG. 12. Several cross-sectional views of PMMA resist pattern exposed to 1×10^{-4} C/cm^2. (a) $CF_4 + O_2$ mixture gas 0.7 Torr, rf power 200 W, using the type B system. (b) $CF_4 + O_2$ mixture gas 5×10^{-2} Torr, rf power 200 W, using the type B system.

On the other hand, the small undercutting under 5×10^{-2}-Torr $CF_4 + O_2$ and 200-W rf power conditions is shown in Fig. 12(b). The normalized lateral etching rate of about 0.1 with 5×10^{-2} Torr suggests high accuracy patterning with this lithographic method.

Figure 13 shows scanning electron microscope (SEM) observations of 0.5-μm-width lines and spaces fabricated in 0.6-μm-thick PMMA film. The resist exposed to 1×10^{-4} C/cm^2 gallium ions is developed by the type B method. In the development, gas pressure and rf power were 5×10^{-2}-Torr $CF_4 + O_2$ and 200 W, respectively.

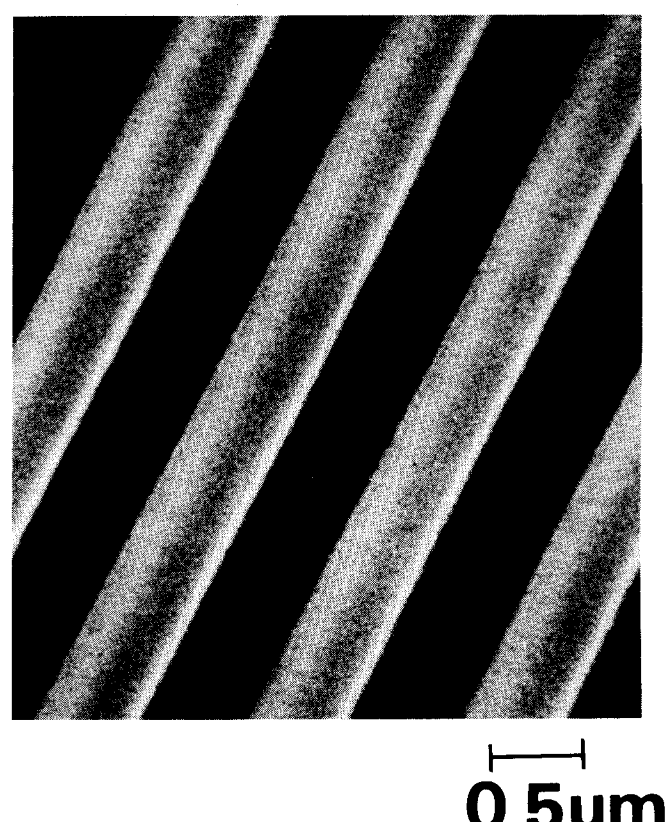

FIG. 13. SEM observations of 0.5-μm-width lines and spaces fabricated in 0.6-μm-thick PMMA film exposed to 1×10^{-4}-C/cm^2 gallium ions. Development conditions: a $CF_4 + O_2$ mixture gas 5×10^{-2} Torr, rf power 200 W, using the type B system.

IV. CONCLUSION

A new lithographic technique employing ion beam exposure and subsequent dry development has been proposed. It has been proved that the etching rate for resists exposed to gallium ions differs from the rate for resists not exposed, when etched by oxygen plasma. The resist sensitivity decreases with oxygen gas pressure. The small thickness of the resist is advantageous from the viewpoint of high sensitivity and high contrast. The resist sensitivity and the contrast value γ, using a $CF_4 + O_2$ mixture for development process, is superior to that using only O_2 gas. The normalized lateral etching rate becomes smaller, as the gas pressure decreases. Patterns using 0.5-μm-width lines and spaces are fabricated in 0.6-μm-thick PMMA film.

This lithographic technique will be important for fabricating minute negative images in other materials.

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